N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286
Volume 5, Number 425 (2017), 5 – 8

UDK 541.138 MC,Ю

A. Mamyrbekova[1], A. Mamitova[1], A. Tukibayeva[1], A. Mamyrbekova[2]

([1]M. Auezov South Kazakhstan state university, Shymkent;
[2]A. Yasawi International kazakh-turkish university, Turkestan, Kazakhstan)
E-mail: aigul_akm@mail.ru

RESEARCH OF PHYSICOCHEMICAL PROPERTIES OF THE DMSO-$Cu(NO_3)_2 \cdot 3H_2O$ SYSTEM

Abstract. Physicochemical properties of the DMSO-$Cu(NO_3)_2 \cdot 3H_2O$ system are studied in the concentration range of 0,01–2 M at 298 K. The refraction index of a solution of copper(II) nitrate in dimethylsulfoxide (DMSO) is measured at 288-318 K. The excess and partial molar volumes of the solvent and dissolved substance are calculated analytically. In work it is demonstrated the good solubility of copper(II) nitrate trihydrate in DMSO at 288-318 K. In diluted solutions, the copper salt is completely ionized. Ion salvation results in the decomposition of the DMSO eigenstructure. Hydrogen bonding between $(CH_3)_2SO$ molecules and the H_2O molecules in the crystallohydrate results in the formation of heteromolecular associates, the number and importance of which in the rearrangement of the liquid phase structure increase as the concentration of the solution grows. The properties of low concentration (<0,4 M) solutions are defined mainly by the properties of DMSO.

Key words: Copper(II) nitrate crystallohydrate, dimethylsulfoxide, solubility, refraction index of solution, solution density.

Introduction. Dimethylsulfoxide (DMSO) molecules are cationotropic, they form quite strong complexes with copper(II) ions that have coordination numbers from 2 to 4. There are data on the formation of stable $[(CH_3)_2SO \cdot NO_3]^-$ complexes in the presence of water when the nitrogen atom is linked directly with the sulfur atom, although the possibility of such bonding was denied in [1]. The existence of $Cu(NO_3)_2 \cdot m$DMSO complexes where m is 2–4 was mentioned in [2].

In this work, we studied the changes in density, viscosity, and refraction index as a function of the concentration of a dissolved substance at 298 K. The refraction index of the DMSO-$Cu(NO_3)_2 \cdot 3H_2O$ system was measured over the wide temperature range of 288-318 K.

Experimental

Copper nitrate crystallohydrate was synthesized according to the procedure described in [3] and recrystallized from water. DMSO was distilled in vacuum (n_D=1,4816, ρ_4=1,0764 г·см^3).The refraction indices of the investigated solutions were measured using an URL model 1 multipurpose laboratory refractometer (accuracy, $5\text{-}10^{-5}$), the density was determined by pycnometry with an accuracy of ±0,5 kg/m^3, and the viscosity was determined using a capillary viscometer with a capillary diameter of 0,59 mm. All measurements were performed at constant temperatures maintained using a UTU-4 multipurpose thermostat with an accuracy of 0,5°C. The content of water in the crystallohydrate rose as the concentration of salt in the DMSO-copper nitrate system grew, and the system was in fact DMSO–$Cu(NO_3)_2 \cdot H_2O$. The presence of small amounts of water (~10 mol %) had no appreciable effect on the physicochemical parameters of dimethylsulfoxide solutions [4] while considerably facilitating the solubility of the salt.

The refraction index and density of a solution of $Cu(NO_3)_2 \cdot 3H_2O$ in DMSO increase as the salt content therein rises (Fig. 1). The isotherms of dependences of the refraction index on the copper(II) nitrate concentration in DMSO are expressed as a broken line (curves 1–5) described by the equation,

$$n = n_0 + b \cdot \lg C, \quad (1)$$

where n_0 is the standard refraction index of a solution obtained by extrapolating n and log$c$ with a straight line to c = 1 M, and b is the slope of the line.

The n_0 and b values (Table 1) were obtained by the least squares processing of the experimental data on a computer. The correlation coefficient for the values determined is in all cases at least 0,95, and the confidence level is 95%.

The relative refraction index–temperature coefficient,

$$E_{n_0} = \left(\partial \lg n_0 / \partial T\right)_c = -2.70 \cdot 10^{-4} K^{-1}, \quad (2)$$

determined from the data from Table 1, lies low in the temperature range of 288–308 K and is close to the *En* of pure DMSO ($-2{,}62 \times 10^{-4}$ K^{-1}). The refraction temperature coefficients of solutions increase in absolute magnitude in the high temperature range (308-318 K) up to $-3{,}6 \times 10^{-4}$ K^{-1}, due obviously to the decomposition of DMSO eigenstructuring. The ionized state of cupric nitrate in solution and the predominant effect of DMSO itself on the optical properties of the system is likely responsible for the slight slope of the n, log$c$ isotherm (b = 0,0068) in the low-concentration range (to 0,4 M).

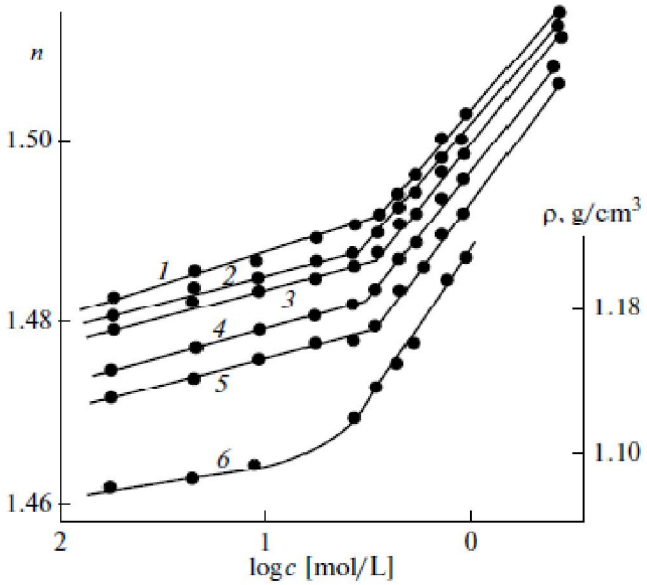

Figure 1 - Refraction index (*1–5*) and density (*6*) of solutions of $Cu(NO_3)_2 \cdot 3H_2O$ in DMSO as a function of the copper salt concentration at (*1*) 288, (*2*) 293, (*3*, *6*) 298, (*4*) 308, and (5) 318 K.

Table 1 - n_0 and b constants of Eq. (1) at different temperatures.
In the ranges of $Cu(NO_3)_2 \cdot 3H_2O$ concentration (0,01 - 4 and 0,4 - 2,8 M)

T, K	n_0	$b \cdot 10^3$	n_0	$b \cdot 10^3$
	0,01- 4 M		0,4 -2,8 M	
288	1,4948	7,176	1,5031	25,304
293	1,4915	6,176	1,5012	24,862
298	1,4902	6,375	1,4997	27,063
308	1,4861	6,850	1,4960	26,797
318	1,4811	5,690	1,4929	29,653

As can be seen from the plot, the slope of the n, log$c$ isotherm increases in more concentrated solutions (>0,4 M); this can be explained by the coarsening of the electrolyte particles induced by ionic association, which is likely enhanced as the temperature rises. In diluted solutions, the rise in density with growing concentration of the solution at a constant temperature of 298 K is also slight (Fig. 1, curve 6). Upon moving to more concentrated solutions (>0,4 M), the slope of the ρ, log$c$ line rises more than eightfold. The high increase in solution density seems to be caused by the ionic association of the electrolyte and the formation of the abovementioned heteromolecular associates, due to the stronger concentration of the solution and the accumulation of water molecules in the crystalline hydrate.

The solubility of copper(II) nitrate in water at 15 and 45°C is 4,4 and 5,3 M, respectively [5]. $Cu(NO_3)_2 \cdot 3H_2O$ crystallohydrate is very soluble in DMSO. We confine ourselves to studying dimethylsulfoxide solutions with concentrations of 2,0 M. The excess and partial molar volumes of the components of the DMSO-$Cu(NO_3)_2 \cdot 3H_2O$ system are given in Table 2 and shown in Fig. 2.

Table 2 - Excess volumes of the DMSO–$Cu(NO_3)_2 \cdot 3H_2O$ system (x_2 is the molar fraction of cupric nitrate)

x_2	$-V_1^E$	$-V_2^E$
0,0013	-0,1200	-0,0704
0,0163	-0,1793	-0,7681
0,0313	-0,3394	-1,2589
0,0462	-0,5955	-1,5442
0,0612	-0,9426	-1,6362
0,0762	-1,3763	-1,5356
0,0912	-1,8917	-1,2471
0,1062	-2,4839	-0,7756
0,1211	-3,1486	-0,1256
0,1361	-3,8804	0,6972
0,1511	-4,6748	1,6888

The partial molar volume of DMSO decreases as the second component is added and curve *1* (Fig. 2) becomes steeper, which can be explained by the transition from one type of the solvent structure to another one. The partial molar volume of $Cu(NO_3)_2$ (Fig. 2, curve *2*) in the investigated concentration range grows linearly as the content of salt in solution rises, due likely to ionization of the dissolved cupric nitrate followed by ionic association.

Conclusion. We have demonstrated the good solubility of copper(II) nitrate trihydrate in DMSO at 288-318 K. In diluted solutions, the copper salt is completely ionized. Ion salvation results in the decomposition of the DMSO eigenstructure. Hydrogen bonding between $(CH_3)_2SO$ molecules and the H_2O molecules in the crystallohydrate results in the formation of heteromolecular associates, the number and importance of which in the rearrangement of the liquid phase structure increase as the concentration of the solution grows.

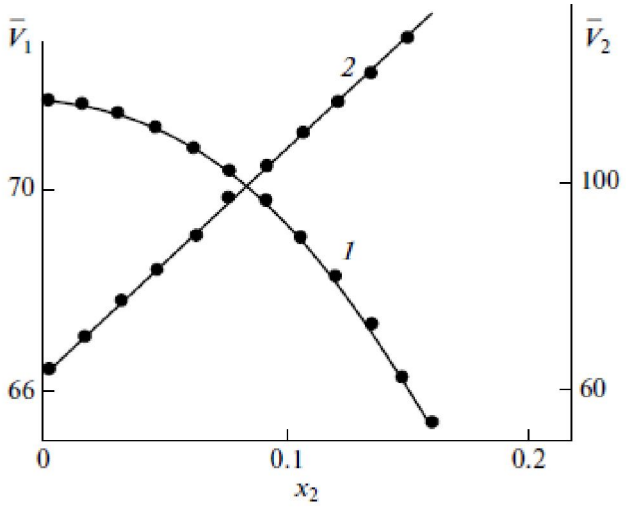

Figure 2 - Partial molar volumes of (*1*) dimethylsulfoxide and (*2*) copper(II) nitrate trihydrate as a function of the composition of a solution at 298 K; x_2 is a molar fraction of the dissolved substance

The properties of low concentration (<0,4 M) solutions are defined mainly by the properties of DMSO. When the temperature rises above 35°C, the structure of the organic solvent decomposes in diluted solutions, the mobility of electrolyte ions increases, and the effect of the solutions' concentration on its optical properties weakens; i.e., the low value of coefficient *b* in Eq. (1) falls further. In solutions

with higher concentrations, the number of heteromolecular associates grows continuously as the salt content in a solution rises, involving the whole system. As a consequence, viscosity increases, ionic association is enhanced, and the effect of concentration on the refraction index of a solution grows.

REFERENCES

[1] Martin D., Hauthal H. Dimethylsulfoxid. Berlin: Academic-Verlag, **1971**. 494 p. (in Russian).

[2] Kukushkin Yu.N. Achievements of the Chemistry of Coordination Compounds. Naukova Dumka, Kiev, **1975**. 248 p. (in Russian).

[3] Karyakin Yu.V. and Angelov I.I. Pure Chemical Reagents. Khimiya, Moscow, **1974.** 408 p. (in Russian).

[4] Karapetyan Yu. A. and Eichis V. N. Physicochemical Properties of Nonaqueous Electrolyte Solutions. Khimiya, Moscow, **1989**. 256 p. (in Russian).

[5] *Chemist's Manual*/Ed. by B. P. Nikol'skii. Khimiya, Moscow, 1964. Vol. 3. 1006 p. (in Russian).

А. Мамырбекова[1], А. Мамитова[1], А. Тукибаева[1], А. Мамырбекова[2]

([1]Южно-Казахстанский государственный университет им. М. Ауэзова, Шымкент;
[2]Международный казахско-турецкий университет им. Х.А. Ясави, Туркестан, Казахстан)

ИССЛЕДОВАНИЕ ФИЗИКО-ХИМИЧЕСКИХ СВОЙСТВ СИСТЕМЫ ДМСО-$Cu(NO_3)_2 \cdot 3H_2O$

Аннотация. Изучены физико-химические свойства – плотность, динамическая вязкость и показатель преломления системы ДМСО-$Cu(NO_3)_2 \cdot 3H_2O$ в интервале концентраций 0,01-2 М при температуре 298 К. Показатель преломления растворов нитрата меди(II) в диметилсульфоксиде (ДМСО) измерен в интервале температур 288-318 К. Аналитическим методом рассчитаны избыточные и парциальные мольные объемы растворителя и растворенного вещества для данной системы. В работе отмечена хорошая растворимость тригидрата нитрата меди(II) в ДМСО в интервале температур 288–318 К. В разбавленных растворах соль меди находится в полностью ионизированном состоянии. Сольватация ионов обусловливает разрушение собственной структуры ДМСО. Вводимые в составе кристаллогидрата молекулы H_2O, взаимодействуя посредством водородной связи с молекулами $(CH_3)_2SO$, приводят к образованию в системе гетеромолекулярных ассоциатов, количество и значение которых в перестройке структуры жидкой фазы повышаются с ростом концентрации раствора. Свойства растворов низких концентраций (<0,4 М) определяются в основном свойствами ДМСО.

Ключевые слова: кристаллогидрат нитрата меди(II), диметилсульфоксид, растворимость, показатель преломления растворов, плотность растворов.

А. Мамырбекова[1], А. Мамитова[1], А. Тукибаева[1], А. Мамырбекова[2]

([1]М. Әуезов атындағы Оңтүстік Қазақстан мемлекеттік университеті, Шымкент;
[2]Қ.А. Ясауи атындағы Халықаралық қазақ-түрік университеті, Түркістан, Қазақстан)

ДМСО-$Cu(NO_3)_2 \cdot 3H_2O$ ЖҮЙЕСІНІҢ ФИЗИКА-ХИМИЯЛЫҚ ҚАСИЕТТЕРІН ЗЕРТТЕУ

Аннотация. ДМСО-$Cu(NO_3)_2 \cdot 3H_2O$ жүйесінің темература 298 К 0,01-2 М концентрация интервалында физика-химиялық қасиеттері - тығыздығы, динамикалық тұтқырлығы және сыну көрсеткіші зерттелген. Диметилсульфоксид (ДМСО) - мыс(II) нитраты ерітінділерінің сыну көрсеткіштері 288-318 К температура аралығында өлшенген. Аналитикалық әдісімен жүйенің құрамындағы еріткіш пен еріген заттың артық және парциальды мольдік көлемдері есептелген. 288–318 К температуралар интервалында диметилсульфоксидте мыс(II) нитраты тригидратының жоғары ерігіштігі байқалған. Сұйытылған ерітінділерінде мыстың тұзы толық ионизирленген күйде болады. Иондардың сольватациясы ДМСО құрылымының бұзылуына негізделген. Кристаллогидраттың құрамындағы H_2O молекулалары $(CH_3)_2SO$ молекулаларымен сутектік байланыс арқылы әрекеттесіп, жүйеде гетеромолекулярлы ассоциаттардың түзілуіне әкеліп, олардың мөлшері ерітінді концентрациясының өсуімен жоғарылап, сұйық фаза құрылымының өзгеруіне әкеледі. Төмен концентрациядағы (<0,4 М) ерітінділердің қасиеттері негізінен ДМСО қасиеттерімен анықталады.

Тірек сөздер: Мыс(II) нитратының кристаллогидраты, диметилсульфоксид, ерігіштік, ерітінділердің сыну көрсеткіші, ерітінділердің тығыздығы.